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POSSIBLE NEW IRDOME MATEFIALS FOR TRANSMISSION TO 4.5-5 MICROME--ETC(U)

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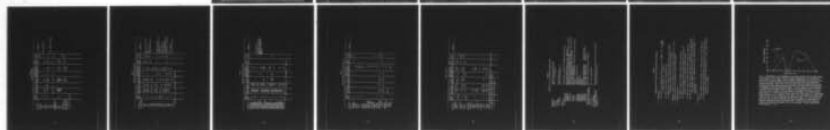
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Possible New Irdome Materials for Transmission to 4.5-5 Micrometers

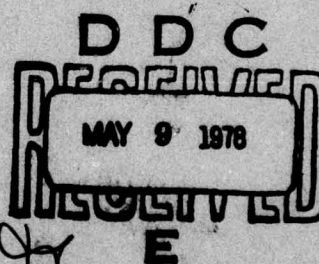
R. W. RICE

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FOREWARD

This report represents a limited updating of a paper by the same title given by the author at the Workshop on Radomes and Irdomes for Tactical Missiles held at the Naval Weapons Center, China Lake, California, 1-4 March 1976.

This paper was also presented by Dr. A. M. Diness for the author at the TTCP Meeting, Subgroup P2 (Ceramics) held in Adelaide, Australia, 14-16 July 1976. Abstracts published in Report TTCP/AUS/P 2/2/76, "Performance and Evaluation of Electro-Ceramic Materials in Military Systems," edited by L. M. Gillin.

POSSIBLE NEW IRDOME MATERIALS FOR TRANSMISSION TO 4.5-5 MICROMETERS

INTRODUCTION

Increasing demands are being placed on irdome materials that can transmit in the 1 to ~ 4.5 to 5 μm region. These increased demands are primarily for substantially greater thermal shock resistance and secondarily for increased rain erosion resistance. Commonly used or proposed alternate IR materials are typically drawn from a limited list of familiar materials that have been studied and/or developed a fair amount which is important for near term development. Table 1 lists some of the common candidates. However, these commonly proposed materials do not offer great improvement over widely used MgF_2 and hence are not expected to meet many future requirements.

The thesis of this paper is thus two-fold. First, that there are many, at least hundreds and possibly thousands of materials that can meet the basic transmission needs. The list of suitable candidates is, of course, greatly reduced as demands for other necessary properties, mainly low, thermal expansion and reasonable hardness and Young's modulus, are considered. Also, as discussed later, the number of candidates can be measurably effected by how close to 5 microns transmission is required. The second thesis is that even with drastic reductions in the number of candidate materials to meet the other requirements, especially low thermal expansion to have good thermal shock resistance, a number of materials that could be much better than the common candidates should be feasible. Therefore, the main purpose of this paper is to present the results of an initial survey to show the potential opportunity of finding better materials, not to be a comprehensive survey to identify final candidates. Thus, the secondary purpose to indentify some areas or materials of opportunity, is meant to be a demonstration of the possible improved materials rather than proposing these specifically, as definite candidates.

Note: Manuscript submitted February 8, 1978.

SURVEY OF MATERIALS

First, for reference, consider the properties of commonly available or used materials for transmission to ~ 5 microns (Table 1). Of the traditional materials, only fused silica has a sufficiently low thermal expansion to have good thermal shock resistance; however, it transmits only to ~ 4 microns and hence is not usable for many applications of interest that typically require transmission to at least 4.5 microns. Further, fused SiO_2 is probably marginal in rain erosion resistance. Note that one of the next lowest transmission materials in this list is alumina; however, its expansion of $\sim 9-10 \times 10^{-6}/^\circ\text{C}$ is high and is, thus, a major factor in its poor thermal shock resistance. Note also the relative high expansion, low hardness, and low Young's modulus of MgF_2 , currently the most commonly used material.

Next, consider the more common non-oxide materials (Table 2). The author knows of no borides or silicides that are dielectric, i.e. that are not electrical conductors, and hence that would be possible dielectric IR transmitting materials. At least two carbides, beryllium carbide and silicon carbide are not intrinsic conductors; however, beryllium carbide is felt to be impractical because of its toxicity and its deliquescence. Silicon carbide is a material currently being given some consideration for IR purposes although it does not give usable transmission completely to 5 microns and it has quite a high index or fraction.¹ Several nitrides may be possible candidates with silicon nitride currently receiving some consideration.¹ However, it only transmits to ~ 4.5 microns and also has a fairly high index or fraction. Many mixed nitride compounds are believed to exist and a substantial number of these may have useful IR transmission, but no data whatsoever, is known about these. Some phosphides should meet the IR transmission requirements but these generally have high indices of refraction. Many sulfides, other chalcogenides, and semi-conductors can also meet the IR requirements but also have high indices of refraction and also sufficiently low hardnesses that most of them have serious rain erosion problems.

Table 3 shows a partial listing of single oxide materials. Transition metal oxides have not been included since data is generally lacking and many are expected to not meet the transmission requirements because of the intrinsic absorption band they have that extends into the IR, e.g. Fig. 1. No really attractive single oxide candidates are seen; the only one of these expected to meet transmission requirements to at least 4.5 microns with a

relatively low expansion is tin oxide. However, its potential as a candidate material is probably limited by its expected fairly high refractive index, its fairly easy reduction, its possible semi-conducting character, and its low Young's modulus and hardness.

A major opportunity for new IR materials is seen to lie in the mixed oxides, primarily the binary oxide systems, i.e., oxide compounds of two metals (Table 4 and 5). There are many families of these materials. Table 4 is only a partial listing of one such family, the aluminates. Many of these materials are expected to meet IR wavelength transmission requirements. Note that amongst this partial listing even with incomplete property determination, there is at least one possible candidate; namely, calcium aluminate with a thermal expansion in the range of 2-3. While possible questions of its stability with H₂O and its general phase stability exist, it does indicate some of the potential of surveying, the wide variety of available materials.

Turning now to a broader survey, Table 5 lists some of the other possible mixed oxide systems that may provide candidate materials, and properties for some of the members of these families. While some borates may be possibilities, it is generally expected that the light weight of the boron atom would make these compounds questionable in their ability to meet the high IR transmission requirement. However, many other systems should meet these requirements. Some of these materials have fairly low thermal expansions, e.g., aluminum niobate and titanium niobate. Two phosphates are known to have rather interesting expansion behavior. First, aluminum phosphate stabilized in the β form has a quite low expansion; unfortunately IR transmission measurements of this material shows that it does not transmit beyond ~ 4 microns² and hence is not suitable. Uranium phosphate, though clearly not of practical interest again illustrates the possibilities of looking beyond typical compounds in that its expansion ranges from a significant contraction to a positive expansion, indicating possibilities of developing very low expansion materials.

Many silicates probably will not meet the transmission requirement since fused SiO₂ itself fails to while corresponding germanates are more likely to because of the heavier germanium atom. However, the silicates generally offer the opportunity for lower expansion. Mullite is a particularly interesting possibility. Tests at the Naval Research Laboratory on transparent hot press samples kindly provided by Dr. J. Mazdiasni of AFML, indicates that this material may be usable to ~ 4.8 microns (Fig. 1). This is one example illustrating the important question of exactly how close to

5 microns transmission is required. Mullite has a relatively low thermal expansion coefficient of ~ 5 and compositions having thermal expansion approaching as low as ~ 3 have apparently been reported though they may possibly have higher silica content which may further compromise the transmission. Besides the above noted hot pressing, the material has been processed as a glass and then crystallized³ with this apparently resulting in strengths as high as 100,000 psi. Thus, this is a particularly good example of the possibilities of looking at new materials. Silicates having a heavy metal ion will generally give broader transmissions, e.g. bismuth titanate and probably zircon transmit closer to 5 microns, though the former and possibly the latter have a fairly high refractive index.

Aluminum titanate illustrates one of the pitfalls one must watch for, namely, this material can have a very low coefficient expansion. However, this is due to opening and closing of microcracks resulting from very anisotropic expansion of the individual crystallites giving apparent low net bulk thermal expansion. However, such microcracking is not tolerable for IR purposes because of the resultant high scattering. Dense, fine grain material, which would not have such microcracking, does not exhibit the desired low thermal expansion. Two other mixed oxide materials, which may have real relatively low thermal expansions, are aluminum and zirconium tungstates, but their phase stability is unknown.

Another possible candidate again illustrating the potential of looking at new materials is calcium zirconate. The literature indicates thermal expansions ranging from approximately 5 to 11. The lower expansion value is reasonably interesting for thermal stress resistance, while the latter is not. Recent tests at NRL indicate a thermal expansion of ~ 7 , which while not low is $\sim 10 - 20\%$ lower than that of magnesia alumina spinel, the only mixed oxide material that appears to have received any consideration for irdomes. Calcium zirconate clearly meets the transmission requirement and its refractory, reasonably hard character as well as some progress in its fabrication (e.g., it is currently skull melted and tests indicate reasonable promise in hot pressing) indicate it might be more promising than spinel.

Table 6 briefly summarizes some of the possibilities seen in this preliminary survey, again emphasizing the mixed oxides as the most substantial area of opportunity with several families of these showing some possibilities. Again it should be emphasized that the number of candidates can be

substantially effected by exactly how far into the IR transmission is required; that is, if transmission is required to 5 microns, few if any of the silicates will meet this, while if transmission to somewhat less than 5 microns is required, then some promising silicates become candidates. Again, mixed nitrides or mixed compounds such as oxinitrides, oxisulfides, carbophosphides, etc., may have some possibilities, but so little is known about these materials that in general they cannot be considered particularly viable candidates, at this time or in the foreseeable future, but should not be totally neglected in a more detailed survey. The recommendation as a result of this consideration is thus that a more detailed survey be made with some accompanying property measurement to fill out the survey and test possible candidate materials in order to select better IR candidates. This should be done in conjunction with designers to more closely determine the exact IR wavelength transmission requirements, since this in fact can be an important factor in considering some possibly attractive candidates, as noted above.

Table 7 summarizes some of the guidelines and pitfalls for a further more detailed survey. Thus, for example, the IR cut-off wavelength, λ , is proportional to the square root of quotient of the effective mass of the ions and the effective spring constant. The spring constant is basically a function of Young's modulus, E , and the effective mass for a diatomic system is simply as shown. It is also important to keep in mind whether the material is cubic or non-cubic; and if non-cubic, the degree of optical and thermal expansion anisotropy. High thermal expansion anisotropy requires fine grain sizes for mechanical integrity. High optical anisotropy may limit the range of usage at shorter wavelengths due to resultant scattering. Note also that while high thermal conductivity will limit thermal stresses under relatively low rates of temperature change, its effect in limiting thermal stress decreases with increasing heating rate, becoming negligible at high rates. Further, high thermal conductivity means higher internal dome or window temperatures which can be detrimental.

SUMMARY AND CONCLUSIONS

This preliminary survey shows that there can be substantial opportunity for improved IR materials amongst compounds consisting of three or more atoms, e.g. with mixed oxide compounds being a good example of the promise of such compounds. It is important that new materials for irdomes and windows have potential for meeting both near and far term needs. The commonly proposed candidates of more de-

veloped materials have, at best, limited potential for needs beyond those of the near term. Thus, a more comprehensive survey-testing program is warranted to investigate the potentially very promising area of new compounds. The focus of attention of this preliminary survey has been materials for use to $\sim 5 \mu\text{m}$. However, it is clear that the possibility of ternary and higher compounds may offer important new materials opportunities for other wave length regions such as 8-14 μm in where mixed halide or mixed chalcogenide materials may be possible candidate families.

ACKNOWLEDGMENT

The support of this work by the Naval Air Systems Command, monitored by Charles Bersch, is gratefully acknowledged.

REFERENCES

1. Private communications, Dr. R. Tanzilli, General Electric Co., Valley Forge, PA.
2. Private communication, Dr. M. Hills, Naval Weapons Center, China Lake, CA.
3. J. F. MacDowell, Corning Glass Works, U. S. Patent No. 1,005,338 (1965).

TABLE I
Typical 1-5 μ m IR Materials

Material	Crystal* Structure	T _M Melting Temp. °C	ρ Density gm/cc	H Hardness kg/mm ²	E Young's Modulus 10 ⁶ psi	α Thermal Exp. Coeff. 10 ⁻⁶ °C ⁻¹	n Refrac- tive Index	IR Cutoff μ m	Comments
Typical IR Materials									
SiO ₂	Glass	> 1500	2.2	800	10	0.5	1.3	4	
MgF ₂	T	1260	3.2	550	16	11	1.3	8	
CaF ₂	C	1360	3.2	150	14	22	1.4	12	
Al ₂ O ₃	H	2050	3.98	2400	60	9-10	1.8	6	
MgO	C	2800	3.58	~ 700	45	13	1.7	9	
CaO-BaO- MgO-Al ₂ O ₃	Glass		3.1	~ 700	20	9-10	1.6	5	

* T: Tetragonal; C: Cubic; H: Hexagonal

TABLE 2
NON-OXIDE CERAMICS

Material	Crystal* Struc- ture	T _m Melting Temp. °C	ρ Density gm/cc	H Hardness kg/mm ²	E Young's Modulus 10 ⁶ psi	α Thermal Exp. Coeff. 10 ⁻⁶ /°C	n Refrac- tive Index	IR Cutoff μm	Comments
Borides									
Carbides									
Be ₂ C									
SiC	C (H)	d~2500	3.2	~3000	65	5	~2.4	<5	toxic deliquescent
Nitrides									
AlN	H	d~2300	3.26	~1300	50	4-6	~2.2		
BN	H		2.2	20-50	3	1-25	low	3?	
Be ₃ N ₂									
GaN									
Si ₃ N ₄	H	d~1900	3.2	2000	45	~5	~2.2	~4.5	toxic, reacts with H ₂ O, O ₂
Mixed Nitrides									
Phosphides									
BP	C	>2000		3200		5-6	3-3.5		
P	H	>2000	3	3800		5-6	2.8		
GaP	C	1620		950		4-5	2.9		
InP	H	~1350		600			3		
Silicides									
Sulfides, other									
Chalcogenides, and Semiconductors				medium to low		medium to high	high	none >5	

* C: Cubic, H: Hexagonal.

TABLE 3

TYPICAL SINGLE OXIDE CERAMICS

Material	Crystal* Structure	T _m Melting Temp. °C	ρ Density g/cm ³	H Hardness kg/mm ²	E Young's Modulus 10 ⁶ psi	α Thermal Exp. Coeff. 10 ⁻⁶ /°C	n Refrac- tive Index	IR Cutoff μm	Comments
Single Oxides									
Al ₂ O ₃	H	2050	3.98	2400	60	9-10	1.8	6	
BaO	C	1920	5.72	<500			~1.9	~20	Very extreme H ₂ O attack.
BaO	H	2530	3.02	1300	57	8-9	~1.6	5-6	Toxic
CaO	C	2600	3.32	<600		12-14		12	Some H ₂ O attack.
CaO ₂	C						~2.2	8	Fairly easy to reduce.
Cr ₂ O ₃	H	4-2000	5.21	~2400		6-8			
GeO ₂	T					~11			
HfO ₂	M	2800	9.68			5-6			
MgO	C	2800	3.58	~700	45	12-13	1.7	~9	Limited H ₂ O attack.
Nb ₂ O ₃	M				25				Variable expansion due to anisotropy
SiO ₂	Glass	~1700		~700	10	0.5		~4	Easily reduced.
SnO ₂	T		7.00			3-5			Extreme H ₂ O attack.
SrO	C	2400		<600		13-14		~17	Limited Radioactivity (α).
TiO ₂	C	3200	9.8		35	9-10		9	Susceptible to reduction.
TiO ₂	T	~1900	4.26	~1000	40	8-9	2.4	5.5	
Y ₂ O ₃	C	2400	4.84	675	26	7-8		8	
ZnO	H		5.66		18	6-7			Easily reduced.
ZrO ₂	T			1500	36	5-6			Requires stabilization.

*H: Hexagonal; C: Cubic; T: Tetragonal; M: Monoclinic.

Table 4
Examples of Aluminate Ceramics

Material	Crystal* Structure	T _m Melting Temp. °C	ρ Density gm/cc	H Hardness kg/mm ²	E Young's Modulus 10 ⁶ psi	α Thermal Exp. Coeff. 10 ⁻⁶ °C ⁻¹	n Refrac- tive Index	IR Cutoff μm	Comments
Aluminates									
BaO·Al ₂ O ₃	C/H	2050	3.99			7-8			
BaO·6Al ₂ O ₃	H	1860	3.64			~8			
BeO·Al ₂ O ₃	O	1880	3.76						
CaO·2Al ₂ O ₃	M	1760	2.90			2-3			
3CaO·5Al ₂ O ₃	O	1720							
CaO·Al ₂ O ₃		1620	2.98						
3CaO·Al ₂ O ₃	C	1540	3.00						
CaO-BaO-MgO- Al ₂ O ₃ glass									
CeO·Al ₂ O ₃	C	2100	3.10		20	9-10			
CaO·Al ₂ O ₃	C	2020	6.17			8-9			
DyAlO ₃	O	2120	4.37	1700		8-9			
Dy ₂ O ₃ ·2Al ₂ O ₃	C	1820	7.70			8-9			
Gd ₂ O ₃ ·Al ₂ O ₃	C	2040	6.05						
FeO·Al ₂ O ₃	C	1440	4.35						
K ₂ O·Al ₂ O ₃	C	>1650							
Li ₂ O·Al ₂ O ₃	C	>1900	2.55			12-13			
Li ₂ O·5Al ₂ O ₃	C		3.60			8-9			
Li ₂ Al ₂ O ₈	C	>1650	3.60	1950	56			5	
MgO·Al ₂ O ₃	C	2130	3.59	1500	35			7	
MnO·Al ₂ O ₃	C	1560	4.12			6-7			
Na ₂ O·Al ₂ O ₃	C	>1700							
NiO·Al ₂ O ₃	C	2030	4.45						
Sm ₂ O ₃ ·Al ₂ O ₃	C	1980							
SrO·Al ₂ O ₃	M	2010							
SrO·2Al ₂ O ₃	C	1660	3.03			6-7			
2Y ₂ O ₃ ·Al ₂ O ₃	C	2040	4.45			8			
3Y ₂ O ₃ ·5Al ₂ O ₃	C	1980							
Y ₂ O ₃ ·Al ₂ O ₃	C		5.50			8-9			
ZnO·Al ₂ O ₃	C	1950	4.58						
* C: Cubic, H: Hexagonal, O: Orthorhombic, M: Monoclinic									

Some H₂O Attack?

Commercial IR material-
good rain erosion resis-
tance (Barr & Stroud
8539B)

Table 5
Some Major Mixed Oxide Ceramic Families

Material	Crystal* Struc- ture	T _M Melting Temp. °C	ρ Density gm/cc	H Hardness kg/mm ²	E Young's Modulus 10 ⁶ psi	α Thermal Exp. Coeff. 10 ⁻⁶ °C ⁻¹	n Refrac- tive Index	IR Cutoff μm	Comments
Borates									
Germanates									
B ₁₂ Ge ₃ O ₁₂	C					7-10	~2	6	
CeGeO ₄	T					5-7			
HfGeO ₄	T					3-5			
ThGeO ₄	T					6-10			
ZrGeO ₄	T					6-9			
Hafnates						4-8			
CaHfO ₃						~3			
Niobates						~10			
Al ₂ O ₃ ·Nb ₂ O ₅						~6			
De ₂ O ₃ ·Nb ₂ O ₅						~2.5			
2MgO·Nb ₂ O ₅						2		<4	
TiO ₂ ·Nb ₂ O ₅						-4-+5		?	
Phosphates						~5		~4.8	
AlPO ₄						~4.5		4-5+	
UO ₂ ·P ₂ O ₅	C								
Silicates									
3Al ₂ O ₃ ·2SiO ₂	O	1800	3.16	~1800	32				
B ₁₂ Si ₃ O ₁₂	C								
ZrSiO ₄	T	d>1750	4.6	~1500	≥24		~2		
Stannates									
3Al ₂ O ₃ ·2SnO ₂		2070				7-8			
BaSnO ₃						9-10			
Zn ₂ SnO ₄						8-9			
La ₂ Sn ₂ O ₇	C								

Table 5 (cont'd)

Material	Crystal* Structure	T _M Melting Temp. °C	ρ Density gm/cc	H Hardness kg/mm ²	E Young's Modulus 10 ⁶ psi	α Thermal Exp. Coeff. 10 ⁻⁶ /°C	n Refrac- tive Index	IR Cutoff μm	Comments
Titanates									
Al ₂ O ₃ ·TiO ₂	O	1860	3.68			0.1**	1.96		
BaTiO ₃	T (C>120°C)	1600	5.9	600±200	18.0	12-13	~2.3	9-11	
Bi ₂ O ₃ ·TiO ₃	O	1975	4.10	~1000		12-13	~2.5	10-127	
CaTiO ₃	C		5.11	~800	45.0	12-13	2.2	~5.5	
SrTiO ₃	T	1250	7.52		~11.0		~2.7	~7.0	
PbTiO ₃	(C>500)								
Rare Earth Titanates									
Tungstates									
Al ₄ W ₅ O ₂	T	1250				~2			
BaWO ₄						17-28			
CaWO ₄	T	2250				17-22			
3La ₂ O ₃ ·WO ₃		2050				~4			
ZrW ₂ O ₈									
Zirconates									
BaZrO ₃	C	2650	6.26			8-0			
CaZrO ₃	C	2400	4.76	600		5-11		~6	
SrZrO ₃	C	2700	5.48		12	10-11			
PbZrO ₃	O	1550	7.42		~17	~10			
**Due to microcracking from very anisotropic expansion; IR windows would have substantially higher expansion.									
*C: Cubic, T: Tetragonal, O: Orthorhombic									

TABLE 6
SUMMARY OF 1-5 μ IR MATERIAL POSSIBILITIES

Materials	Opportunities and Limitations
BORIDES	None - no transmission
NITRIDES	
a) single	Possibly AlN or GaN
b) mixed	May be some possibilities
OXIDES	
a) single	Possibly SnO ₂ , probably no transition metal oxides
b) mixed oxides	
aluminates	May be good possibilities, e.g. Ca aluminates
bismuthates	Unknown-but may be promising though higher refractive indices
borates	Doubtful that any will transmit to 5 μ
germanates	May be good possibilities-better transmission than silicates, but higher expansion and refractive indices
hafnates	May be some possibilities
halides	Doubtful - high expansion, low hardness, and often moisture attack
niobates	May be some possibilities
phosphates	Uncertain
silicates	Probably none
stannates	Uncertain
tantalates	Unknown
titanates	May be some possibilities
tungstates	May be good possibilities
zirconates	May be some possibilities
Phosphides, Chalcogenides and Semiconductors	Opportunity, but high refractive indices
Silicides	None - no transmission
MIXED COMPOUNDS	
(e.g. Oxynitrides, oxy-sulfides, carbophosphides, etc.)	May be possibilities, but least known area of material properties and preparation

TABLE 7

GUIDELINES AND PITFALLS FOR NEW CANDIDATE IR MATERIALS

1. Transmission

(a) longer wave transmission with heavier ions $\lambda \propto \sqrt{M/k}$ $k \propto E$, $M = \frac{m_1 m_2}{m_1 + m_2}$;
 $E = \text{Young's Modulus}$, $m_i = \text{ion masses}$

(b) heavier ions increase refractivities index

(c) compounds with transition metal ions probably won't give necessary transmission because of intrinsic visible-IR absorption

2. Hardness - often not as critical, can be increased by alloying; e.g. fifty to several hundred percent, especially in ionic bonded systems.

3. Thermal Expansion

(a) expansion tends to be lower for higher melting materials

(b) expansion generally increases with increasing ionic bonding and generally decreases with increasing covalent bonding

(c) expansion tends to increase with decreasing valence of a given ion

(d) some low expansion coefficients are due to accommodation of highly anisotropic crystal expansion by cracks and pores. Also, some materials with low expansion at lower temperatures have high expansions at higher temperatures

4. Stability

(a) some compounds are not stable, e.g. undergo reduction or decomposition

(b) some undergo phase transformations between different crystal structures; some can be stabilized in a more desirable, e.g. lower thermal expansion structure by "alloying"

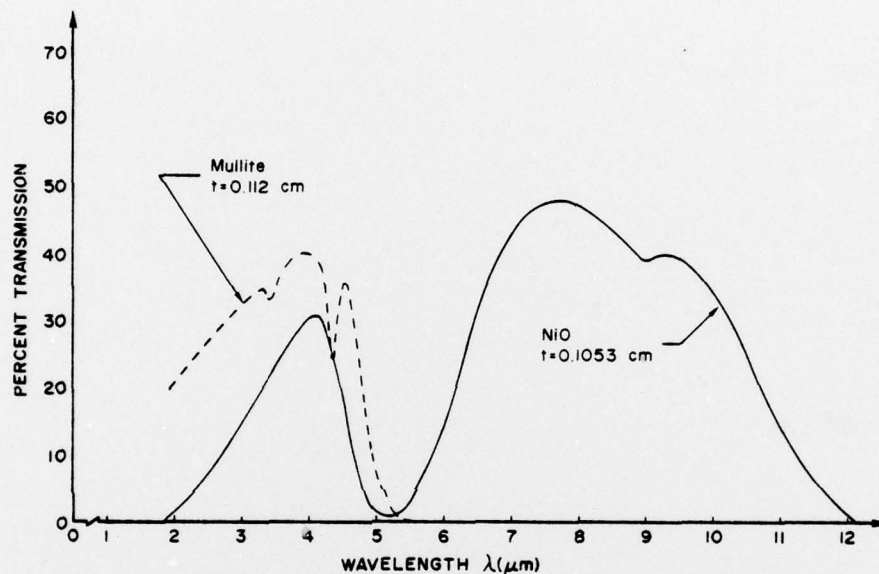


Fig. 1 — Transmission of polycrystalline (hot pressed) mullite and NiO single crystal as a function of wave length. While the mullite transmission is not corrected for surface reflections, the primary factor limiting its transmission is trace porosity left from the hot pressing operation which could be greatly reduced by further processing improvement. Since much of the porosity is quite fine, scattering from this increases as the wave length decreases and hence is the major factor in the drop-off in transmission with decreasing wave length. A critical question for the application of mullite for IR purposes is what the source of the absorption band at $\sim 4.4 \mu\text{m}$ is and the extent to which it may be reduced or eliminated. The Verneuil grown NiO crystals ($\rho \sim 7 \times 10^6$ ohm-cm) data is from R. W. Johnson and D. C. Cronmeyer, Physical Review 93, 3, p. 634-635, 1 Feb 1954. The wave lengths of the short wave length cut off ($\sim 2 \mu\text{m}$ for NiO) and the absorption band ($\sim 5 + \mu\text{m}$ for NiO) will vary some with the type of material. However, these effects are characteristic of transition metal oxides which thus makes most, or possibly, all such compounds unlikely candidates for IR usage in the 1 to 5 μm region. Note the thickness for both samples is $\sim 1 \mu\text{m}$.